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Steve W. Martin

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Department of Materials Science & Engineering
2220 Hoover Hall
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A new research project was initiated to investigate whether high proton conductivity chalcogenide glasses could be prepared by doping base chalcogenide glasses, like glass B2S3 with a proton source, like H2S to yield proton conducting membranes for use in intermediate temperature proton exchange membrane fuel cells. While it will be shown below that indeed proton doped chalcogenide glasses could be prepared over wide ranges of compositions from a number of different base chalcogenide glasses, including B2S3, the proton conductivity for all of these glasses and in some cases polycrystals, was always quite low, rarely exceeding 10-5 (S/cm) at 100 oC. In addition, the proton doped glasses and ceramics exhibited limited thermal stability such that these materials thermally decomposed rapidly losing H2S, the proton source, above 100 oC and for this reason had very limited usefulness above 100oC.

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| **Authorizing Signatures:** | _____<br>Steve W. Martin<br>515-294-0745<br>swmartin@iastate.edu |

**Executive Summary:**

A new research project was initiated to investigate whether high proton conductivity chalcogenide glasses could be prepared by doping base chalcogenide glasses, like glass $B_2S_3$ with a proton source, like $H_2S$ to yield proton conducting membranes for use in intermediate temperature proton exchange membrane fuel cells. While it will be shown below that indeed proton doped chalcogenide glasses could be prepared over wide ranges of compositions from a number of different base chalcogenide glasses, including $B_2S_3$, the proton conductivity for all of these glasses and in some cases polycrystals, was always quite low, rarely exceeding $10^{-5}$ (S/cm) at 100 °C. In addition, the proton doped glasses and ceramics exhibited limited thermal stability such that these materials thermally decomposed rapidly losing $H_2S$, the proton source, above 100 °C and for this reason had very limited usefulness above 100°C.

Protonated thioborate phases were successfully prepared by reacting vitreous $B_2S_3$ ($\nu$-$B_2S_3$) with $H_2S$. This reaction yielded polycrystalline meta-thioboric acid $(HBS_2)_3$ as vapor condensates.

$$3/2B_2S_3 + 3/2H_2S \rightarrow c\text{-}(HBS_2)_3 \quad (1)$$

$HBS_2$ has 3-connected borate units ($BS_3$). The structure is predominantly made of ring units consisting of three $BS_3$ units with all external sulfur atom terminated by proton ($(B_3S_3)(SH)_3$ units) and some isolated planar trigonal units with one non-bridging sulfur atom ($BS_{2/2}SH$ units).

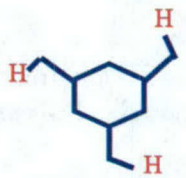


**Figure 1.** Structure of metathioboric acid $c$-$(HBS_2)_3$

Although $HBS_2$ is rich in anhydrous protons (50 mol. % $H_2S$ modification) its thermal stability is low and has a melting point of only 130 °C, further it is a molecular solid and could not be quenched to form glassy phase. Hence materials such as S, $B_2S_3$ and $GeS_2$, etc were added to thermally stabilize the materials and to achieve high proton conductivity. The main aim of the study is to obtain fast proton conducting (FPC) sulfide glasses analogous to fast ion conducting oxide glasses of the family MX+$M_2O$+FxOy; where MX is metal halide (X = I, Cl, Br), M = Ag, Li, Na, etc and FxOy is glass forming oxides such as $B_2O_3$, $SiO_2$, $GeO_2$, etc. Accordingly, FPC sulfide glasses will have a general formula, **HX + $H_2S$ + FxSy**; where, FxSy is the glass forming sulfide $B_2S_3$, $GeS_2$, etc. Efforts were specifically made to obtain glasses and glass-ceramic materials in different class as listed below.

i. **Proton modified binary systems with general formula, $H_2S$ + FxSy**
ii. **Pseudo-binary systems with two glass-forming sulfides, to study mixed glass former effect, with general formula $H_2S$ + FxSy + Fx'Sy'**
iii. **Complex ternary system with general formula**

**HX + $H_2S$ + FxSy** - *In-situ* creation of H-X phases using metal halides $SnI_2$, $SnI_4$, $GeI_2$, etc.
**MX + $H_2S$ + FxSy** - Interstitial doping of MX phases MX – CsI, RbI, etc
**MS + $H_2S$ + FxSy** – Structural modification my alkaline sulfides MS = SrS, BaS, etc.

Several new series of novel proton conductors with interesting structural features have been prepared. Good improvements in proton were obtained towards targeted conductivity values. The results obtained in each class of these materials are described below.

**Summary of Results Obtained from the Research Project**

**1. Proton modified binary systems with general formula, $H_2S$ + FxSy**

Samples in this series where obtained by reacting $HBS_2$ with $B_2S_3$ and S. The reactions were carried out in sealed silica tube and melt in the tube was quenched in cold water to obtain glass and glass ceramic phase. Efforts were also made to obtain new thio-acids as described below.

**1.1. $xH_2S + (1\text{-}x)B_2S_3$ series**

Samples in this series were obtained by reacting $B_2S_3$ and $HBS_2$ according to the general reaction scheme,

$$(2x)HBS_2 + (1\text{-}2x)B_2S_3 \rightarrow (x)H_2S + (1\text{-}x)B_2S_3, \text{ with } 0.0 \leq x \leq 0.5 \qquad (2)$$

The glass forming region and structural species involved in this series are shown in Fig. (2).

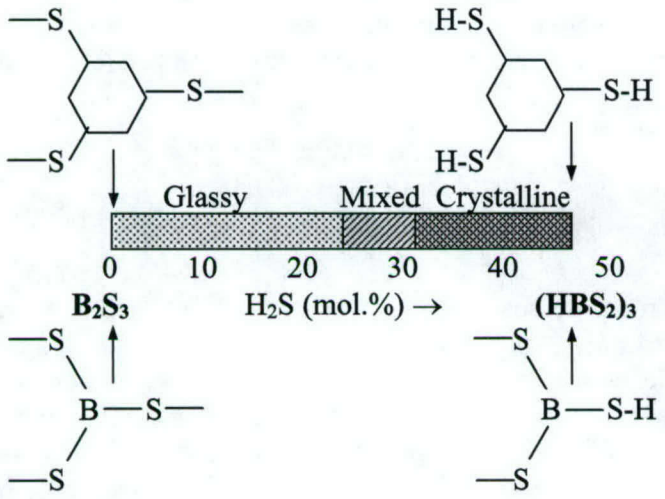


**Figure 2.** Glass formation region in $H_2S + B_2S_3$ series.

The density of these glasses remains practically unaffected by addition of $H_2S$. The glass transition temperature, however, was found to decrease significantly with the addition of hydrogen sulfide to $B_2S_3$. The IR and Raman spectra suggest that that these glasses are comprised of trigonal borate units and 6-membered rings. Unlike other alkali modified borate glasses, no tetrahedral groups upon addition of $H_2S$ to $B_2S_3$ are formed. The $^{11}B$ NMR spectra are also consistent with the coordination of borate units. The material prepared here shows that it is possible to protonate chalcogenide glasses in an anhydrous form.

The protons in $HBS_2$ are bonded covalently and the migration of $H^+$ ion is hard to achieve unless other support mechanisms are available. While many solids are poor conductors in the crystalline form they can be very good ionic conductors in glassy form. In an analogous way, glasses of the protonated materials have been prepared here. The free volume and the interstitial sites available in the glassy phase promote ion migration, as it will be seen later in this section. The temperature

dependence of proton conductivity below glass transition temperature / melting point of the glassy and ceramic samples in the binary x $H_2S$ + (1-x) $HBS_2$ is shown in Fig. (3).

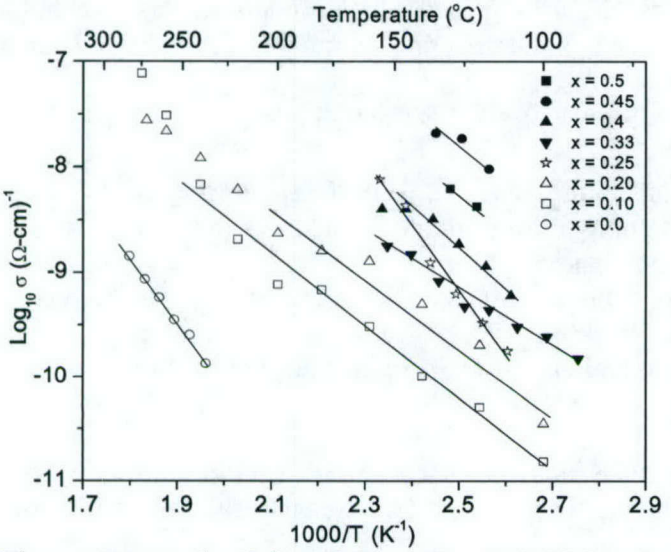


**Figure 3.** Proton conductivity of the samples in the x $H_2S$ + (1-x) $B_2S_3$ series, below glass transition temperature / melting point of the samples.

The proton conductivity of the protonated thioborate glasses is found to be around $10^{-11}$ to $10^{-7}$ $Scm^{-1}$ in the temperature range of 80 °C to 280 °C. In *c*-$HBS_2$ the conductivity decreases after the melting point (140 °C). This is because the *c*-$HBS_2$ loses $H_2S$ similar to the dehydration found in hydrous acids and the proton conductivity decreases sharply. The IR studies of the heat-treated samples (for temperature > 140 °C) have shown that the heat treatment removes most but not all of the protons. The remaining protons give raise to significantly lower ionic conductivity at higher temperatures (> 220 °C). The samples in the range $0.5 < x < 0.25$, similar conductivity behavior is observed, however these samples are thermally more stable than *c*-$HBS_2$. The protonated glass with 25% $H_2S$ + 75% $B_2S_3$ has slightly lower conductivity at temperatures below 120 °C, but the conductivity increases with temperature up to $T_g$. The conductivity of this sample decreases after the glass transition temperature (155 °C) due to the loss of a significant proportion of its protons. Samples with lower proton concentration ($0.1 < x < 0.2$) have lower conductivities at lower temperature. However these samples have better proton conductivity at higher temperature since the glass transition temperature of these samples are higher. The *v*-$B_2S_3$ also exhibits some proton conductivity due to a small concentration of proton present in them (see IR spectra in previous section). The activation energy for the proton migration is found to be around 1.0 to 1.2 eV

### 1.2. $H_xB_yS_z$ series

Samples in this series were obtained by reacting sulfur and $HBS_2$ according to the general reaction scheme,

$$HBS_2 + S \rightarrow H_xB_yS_z \qquad (3)$$

These samples were obtained as crystalline samples. The proton conductivity measurements showed no improvement in conductivity although these samples thermally more stable than $HBS_2$.

### 1.3. Preparation of thio-aluminic acid, $H_2S + Al_2S_3$.

Protonation of thio-alumina were initially tried by using metallic aluminum powers in a silica reactor set up in glove-box. $H_2S$ was passed though the melt of aluminum to form aluminic acid according to,

$$2Al + 2H_2S \rightarrow 2(HAlS_2) + H_2\uparrow \rightarrow Al_2S_3 + H_2S\uparrow \quad (4)$$

These reactions were carried out at a temperature of about 700 °C and owing to this high temperature aluminic acid immediately decomposed to form a more stable $Al_2S_3$ in the crucible. However, some protonated alumina could be obtained as vapor condensates at the upper cooler part of the reactor. The IR spectrum of this sample has shown S-H band at indicate the proton present in the sample. However the intensity of this peak is weak due to poor protonation. Reactions were carried to increase the protonation and to increase the yield of aluminic acid however no improvement in yield could be obtained.

Reactions are now being carried out to prepare aluminic acid starting from aluminum halides ($AlX_3$) at low temperature under pressurized conditions. These reactions are carried out according to the following scheme,

$$AlX_3 + 2H_2S \rightarrow HAlS_2 + 3\ HX\uparrow \quad (5)$$

### 1.4. Preparation of thio-silicic acid, $H_2S + SiS_2$.

Thio-silicic acid is expected to be thermally more stable than borate system owing to the higher melting point of $SiS_2$ and its tetrahededral coordination. Reactions were initially carried out to protonate thio-silicate at high pressure (RT pressure 30 to 60 psig) at elevated temperature (200 – 400 °C) for long periods of time (1 – 4 days). However these reactions resulted in no protonation of the silicate. Similar reactions with further increase in pressure and temperature will be carried out to protonate thio-silicate.

Reactions by bubbling $H_2S$ through hot thio-silicate (650 °C) have also been carried out and this route produced white spongy condensates. This indicates possibility of thio-silicic acid preparation by this route. The IR spectrum of a white vapor condensate shows the S-H stretch modes and indicates the proton present in the sample. However, the low intensity of this peak suggests low proton concentration. More reactions are being carried to increase the proton concentration and to increase the yield.

Poly iodide route for the preparation of thio-silicic acid is also being explored for the preparation of thio-silicic acid. The expected reaction scheme for this route is shown below,

$$SiI_4 + 3H_2S \rightarrow H_2SiS_3 + 4HI\uparrow \quad (6)$$

**1.5. $H_2S + As_2S_3$** Protonation was also successfully carried out in arsenate. However the conductivity of these materials is found to be very low (see previous reports for details).

**2. Pseudo-binary systems with two glass-forming sulfides, to study mixed glass former effect, with general formula $H_2S$ + FxSy + Fx'Sy'**

The pseudo-binary systems were studied to improve proton conductivity of the samples and to increase the glass forming ability. The second glass former Fx'Sy' which has higher melting point compared to boron sulfide such as $GeS_2$ and $SiS_2$ and second glass formers which has comparable melting point such as $As_2S_3$ and $P_2S_5$ were prepared by sealed tube reactions and studied.

**2.1. $H_2S$-$GeS_2$-$B_2S_3$ system.**

In the mixed former system ($B_2S_3$+$GeS_2$), the second glass former $GeS_2$ extends the glass-forming region to about 40 mol.% of $H_2S$. This is due to the additional networking linkages provided by the tetrahedral structure of the germanate units. The density of the samples in the $H_2S$ + $B_2S_3$ series do not vary much and they remain close to that of the host material ($B_2S_3$, density 1.71 g/cm$^3$). However, in the pseudo-binary borogermanate series the density decrease with protonation or in other words increase with $GeS_2$ substitution. This decrease is presumably influenced by the substitution of the heavier $GeS_2$ for the lighter $B_2S_3$ in the lower density $HBS_2$.

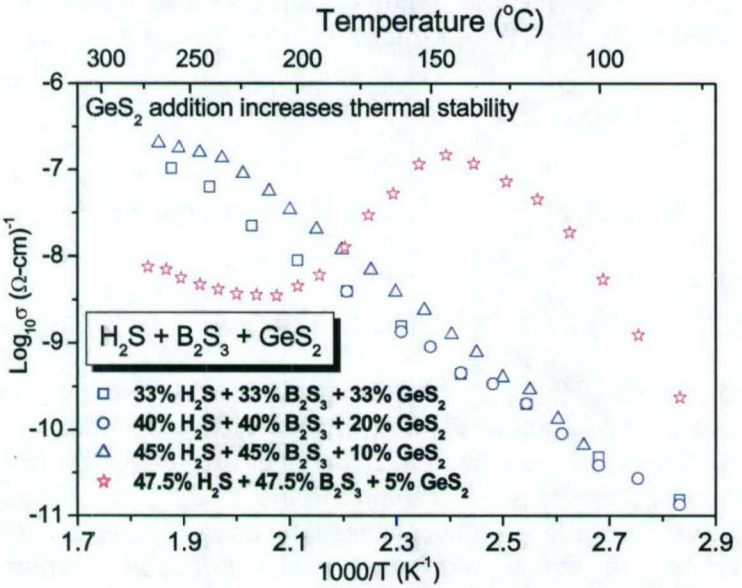


**Figure 4.** Proton conductivity of the samples in the $H_2S$ + $B_2S_3$ + $GeS_2$ series.

The proton conductivity of some of the sample in this series has been already reported in last year. Conductivity measurements of more samples were carried out as are shown in Fig. (4). The sample with 5% $GeS_2$ content shows good improvement in conductivity compared to $HBS_2$. However, this sample had lower thermal stability and loses its proton conductivity at about 150 C. In the ternary glass compound with 33% $H_2S$ + 33% $B_2S_3$ + 33% $GeS_2$, the conductivity is stable over a wide range of temperature because the $T_g$ of this glass is higher. Below $T_g$, the proton conductivity is of the order of $10^{-7}$ S cm$^{-1}$. The activation energy of this sample is ~ 0.83 eV. This is lower than the activation energy of 1.2 eV found in the 25% $H_2S$ + 75% $B_2S_3$ glass. Thus the addition of $GeS_2$ not only increases the stability of the glasses over a higher temperature ranges but also increases the conductivity by lowering the activation energy. Such a "mixed

former effect" has also been observed in other mixed chalcogenide glass forming systems before. However, the exact nature of the structural basis for this effect is not known at this time.

In the ternary borogermanate system, the proton conductivity is found to be at least an order more than that of the samples in the binary system and more importantly, also found to be more thermally stable.

### 2.2. $H_2S$-$B_2S_3$-$As_2S_3$ system.

Several good glasses with high proton concentration were prepared by adding $As_2S_3$ to $HBS_2$. The following glasses were prepared in this mixed former system,

$$05\%\ As_2S_3 + 95\%\ HBS_2 \rightarrow 47.5\%\ H_2S + 47.5\%\ B_2S_3 + 05\%\ As_2S_3$$
$$10\%\ As_2S_3 + 90\%\ HBS_2 \rightarrow 45.0\%\ H_2S + 45.0\%\ B_2S_3 + 10\%\ As_2S_3$$
$$15\%\ As_2S_3 + 85\%\ HBS_2 \rightarrow 42.5\%\ H_2S + 42.5\%\ B_2S_3 + 15\%\ As_2S_3$$
$$20\%\ As_2S_3 + 80\%\ HBS_2 \rightarrow 40.0\%\ H_2S + 40.0\%\ B_2S_3 + 20\%\ As_2S_3$$

The improved glass formation was owing to the good glass forming ability of the arsenate. However, these glasses had no significant improvement in proton conductivity compared to the binary $H_2S + B_2S_3$ system. The structural analysis of these samples is being carried and will be reported soon.

### 2.3. $H_2S$-$B_2S_3$-$P_2S_5$ system.

A new series of ceramics were prepared by adding thioboric acid with phosphorus sulfide. $P_2S_5$ was added to $HBS_2$ according to

$$x\ P_2S_5 + (1\text{-}x)\ HBS_2 \rightarrow ((1\text{-}x)/2)\ H_2S + ((1\text{-}x)/2)\ B_2S_3 + x\ P_2S_5;\ x = 0.1, 0.2, 0.3. \quad (7)$$

The IR spectra of samples in the $x\ P_2S_5 + (1\text{-}x)\ HBS_2$ series has shown bands from ~500-625 $cm^{-1}$ in this series indicating the presence of P-S vibrational modes. No evidence of tetrahedral borons or four-membered rings can be seen, suggesting that the compounds are similar to $HBS_2$ in basic coordination geometry. Conductivity results for the samples in the $(x)\ P_2S_5+(1\text{-}x)\ HBS_2$ series show several sections with different slopes indicating changes in conduction mechanisms or structural transformation. The sample with, x=0.1 produced a large hump in conductivity around 100°C and dropping suddenly at 209°C. This indicated the decomposition of the sample after 210°C, exhibiting exceptionally high proton conduction below 210°C. The hump was not seen on the second run confirming the fact that most of the mobile protons were lost. Similar behavior was observed when x=0.2 however increase in slope was not as drastic and the discontinuity was not clearly seen.

Recently samples in this series were also prepared by reacting $HBS_2$ and $P_2S_5$ in liquid $H_2S$ under its vapor pressure conditions (~270-280 psig). This reaction yielded a mixed system in crystalline phase. The proton conductivity of the sample with a composition 37.5% $H_2S$+37.5%$B_2S_3$+25%$P_2S_5$ is shown in Fig. (5) with different electrodes. Very good improvement in conductivity is obtained compared to the precursor. This is very encouraging

improvement in conductivity towards the targeted conductivity value of about $10^{-3}$ $Scm^{-1}$. Further studies on structural determination and compositional variations are under progress.

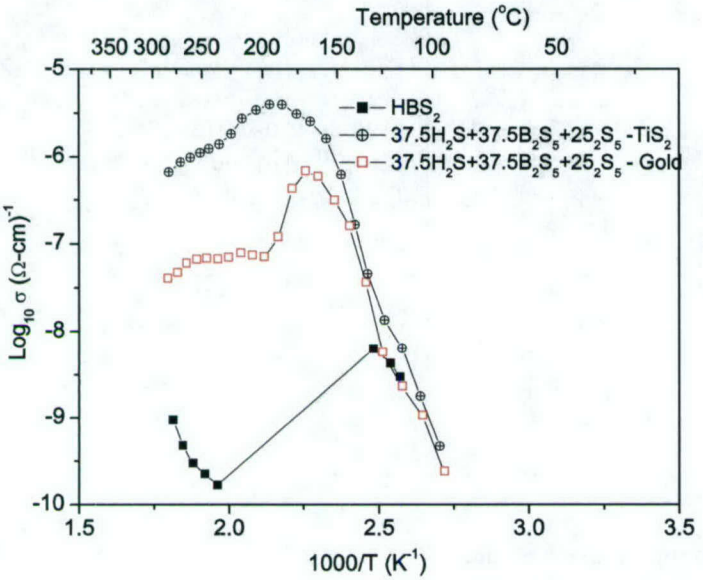


**Figure 5.** Proton conductivity of the samples in the x $P_2S_5$ + (1-x) $HBS_2$ series.

### 2.4. $H_2S$-$B_2S_3$-$SiS_2$ system.

Mixed glass forming borosilicate system, $H_2S + B_2S_3 + SiS_2$ has also been carried out to improve thermal stability of the system owing to high melting point of thio-silicate. Fine powders of $HBS_2$ and $SiS_2$ are mixed, loaded in a silica tube, and sealed. The sealed tube was heated to about 500 to 700 °C depending on the composition of the mixture to obtain a uniform melt. The tube with molten mixture was then quenched in water to obtain protonated glassy or ceramic phases. Samples with the following molar composition have been prepared,

$$y\%\ SiS_2 + (100\text{-}y)\%\ HBS_2 \rightarrow (100\text{-}y)/2\%\ [H_2S + B_2S_3] + y\%\ SiS_2, \text{ with } y = 5, 10\%. \quad (8)$$

Glassy samples are obtained by adding $SiS_2$ to $HBS_2$ and the glass formation is mainly due to the additional network connection provided by the tetrahedrally coordinated thiosilicate. The IR spectra of these samples are shown in Fig. (6). The glassy nature of the samples is responsible for broad IR bands in this system. Decrease in the intensity of rings mode at 1000 $cm^{-1}$ is seen with the addition of $SiS_2$ to $HBS_2$. This decrease in intensity of the ring mode is due to its break-up and consequent polymerization of the network by silicate units leads to an amorphous phase. A new broad band around 500 $cm^{-1}$ appears upon addition of $SiS_2$ and its intensity increases with $SiS_2$ content in the sample. This band is attributed to $SiS_4$ tetrahedra. The IR and Raman spectrum of the pure thiosilicate has several $SiS_4$ modes arising from edge-shared, corner shared silicate units in different structural species (E1 and E2 modes). However, silicate modes in the present ternary glass appear less complex. This is due to the lower molar concentration $SiS_2$ in the system and subsequent absence of other complicated inter-tetrahedral linkages that are otherwise possible in pure thiosilicate.

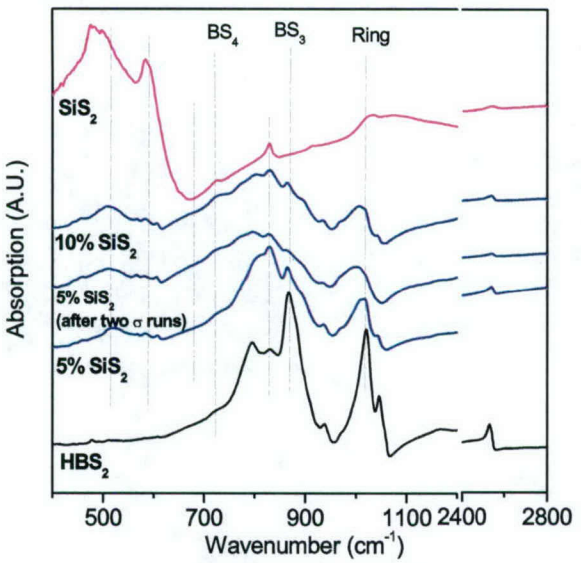


**Figure 6.** Infrared spectra of the samples in the $H_2S$ + $B_2S_3$ + $SiS_2$.

In the $H_2S$ + $B_2S_3$ + $SiS_2$ ternary system with mixed formers, the conductivity is found to be low in the temperature range of 100 to 150 °C compared to the binary thioboric acid (50% $H_2S$ + 50% $B_2S_3$) (see Fig. (7)). However, these samples have higher melting points and the conductivity increases with temperature and reaches good conductivity at temperatures > 150 °C. The activation energy for proton migration in $H_2S$ + $B_2S_3$ + $SiS_2$ system is found to be ~ 1 eV. Proton in this mixed system is either bonded with borate or silicates structural units. However, the extent of proton distribution in different environment is not known at this time. $SiS_2$ has higher melting point and also the corresponding binary thiosilicic acid is anticipated to have higher melting point than boric acid. This is probably the cause for improved thermal stability of the glasses in the $H_2S$ + $B_2S_3$ + $SiS_2$ ternary system.

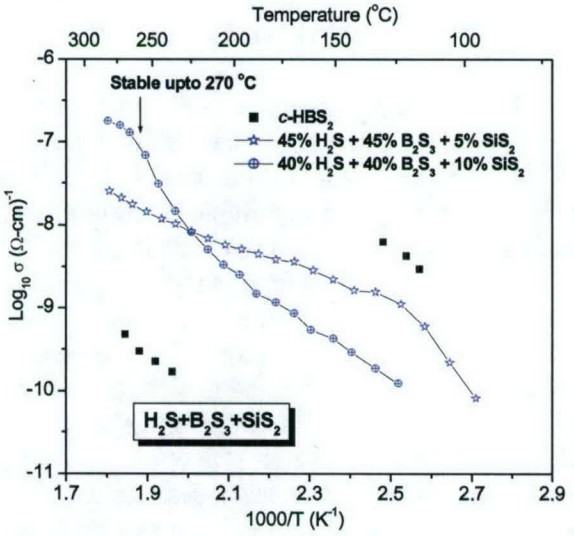


**Figure 7** Proton conductivity of the samples in the $H_2S$ + $B_2S_3$ + $SiS_2$.

## 3. Complex ternary systems

### 3.1. *In-Situ* creation of H-I phases by metal halide doping

As shown earlier, adding meta-thioboric acid, $(HBS_2)_3$, to $B_2S_3$ produces protonated glasses. The conductivity measurements of these glasses showed significant proton conductivity, however the magnitude of the conductivity is very low to be considered for PEM fuel cell applications. In an effort to increase the conductivity it was proposed to incorporate hydrogen iodide bonding into the glass melts. These glasses would be analogous to other fast ion conducting glasses doped with AgI, LiI, etc.

The difference between the other doping materials and HI is the fact that hydrogen iodide is a gas at ambient conditions. Therefore, it is not as simple to dope the glasses with HI as it is with AgI or LiI. There are several different proposed methods for which H-I bonding might be incorporated into the system. (i) Bubbling through the glass melt, (ii) using a liquid phase absorption synthesis, or (iii) through a displacement reaction with another metal halide (i.e. $PbI_2$, $SnI_2$, $SnI_4$, $GeI_4$, etc.). One possible reaction for such a displacement reaction is shown below in Eq. (9)

$$SnI_2 + (HBS_2)_3 \rightarrow SnS(B_3S_3)S_{2/2}SH \qquad (9)$$

In the displacement reactions the cation should be able to displace the proton and then bond to a sulfur atom. This would also mean that at least one of the iodine atoms would be released and should attract the displaced proton, thereby creating H-I *in-situ*. For the initial trials of these reactions it was decided to dope the materials with metal halide salts $SnI_4$ and $SnI_2$.

#### 3.1.1. $SnI_4 + HBS_2$ system

The series of compounds in this system were prepared according to, (x) $SnI_4$ + (1-x) $(HBS_2)_3$. These reactions were carried out for x = 0.05, 0.1, 0.15, 0.2, 0.35, and 0.5. A fine powder of each component was weighed out, mixed, and poured into a silica tube. The tube was then sealed under vacuum. The tubes were then heated to 200-220 °C at 2 °C/min. These melts were homogeneous and light red in color. Different compositions of the melt were quenched in air and in water, to aid glass formation. However, the resultant product was polycrystalline. DSC, IR, and Raman were used to characterize the samples. The DSC curves of these samples indicate that the $SnI_4$ and $HBS_2$ mixtures begin melting at about 80 °C and hence these materials will not be useful for the higher temperature applications. The conductivity measurements also show immeasurable resistance until the sample begins to melt around 80 °C.

Fig. (8) shows the Raman spectra of these samples. The very strong peak at 147 $cm^{-1}$ is indicative of the $A_1$ symmetry of $SnI_4$. The two peaks at 209 and 213 $cm^{-1}$ are attributed to the E and $F_2$ symmetry of $SnI_4$ crystals respectively. The other important peak at 2539 $cm^{-1}$ indicates the presence of S-H. The spectra show that the addition of just a small molar fraction of $SnI_4$ greatly reduces the S-H peak intensity. In addition, the strong $A_1$ peak for $SnI_4$ is very strong

even at 10 molar%. This is attributed to the large difference in molecular weights between $SnI_4$ and $HBS_2$. Ten molar percent $SnI_4$ is equivalent to almost 50 weight%. The spectra indicate that there are no new peaks suggesting that the two compounds form a simple solid solution.

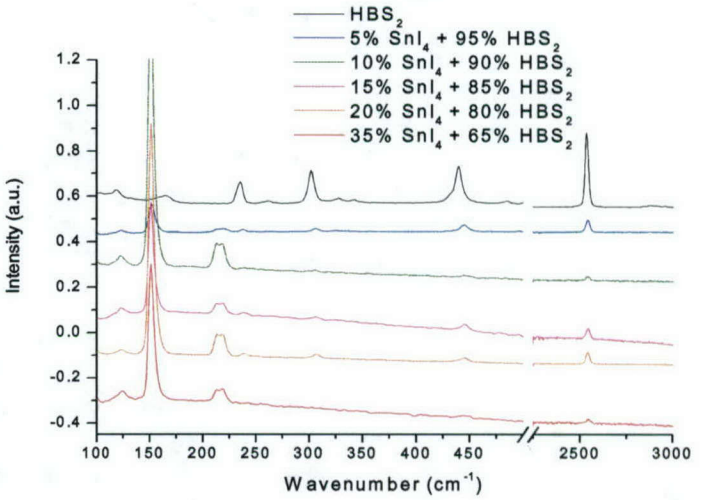


**Figure 8.** Raman spectra of samples in the series of $SnI_4$ + $HBS_2$.

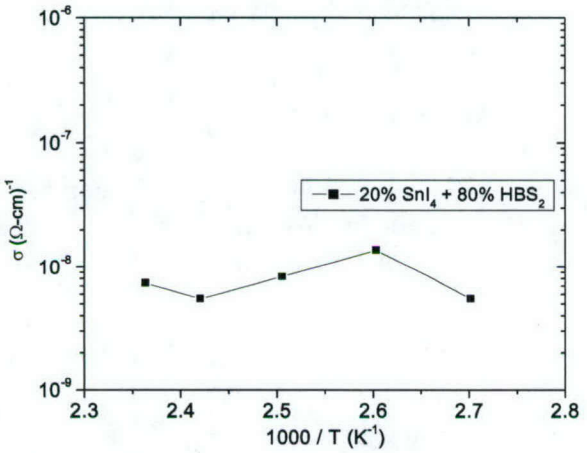


**Figure 9** Conductivity of $SnI_4$ + $HBS_2$. The sample melts around 115 °C or 2.6 on this graph.

### 3.1.2. $SnI_2$ + $HBS_2$ system

The series of compounds in this system were prepared according to, (x) $SnI_2$ + (1-x) $(HBS_2)_3$ These reactions were carried out for x = 0.1, 0.2, and 0.33. A fine powder of each component was weighed out, mixed, and poured into a silica tube and sealed under vacuum. Samples were heated to between 150 and 400 °C depending on the composition. The samples showed some indication of melting but could form a good homogeneous melt. The sample with x = 0.1 was heated to 325 °C, after 20 hours a semi solid had formed on the bottom. Turning the tube upside down and then quenching separated the solid and liquid parts. The solidified liquid portion (reddish-orange polycrystals) and the bottom portion (light brown color) were separated. The x = 0.1 and 0.2 were also heated in a different manner. The samples were heated to 950 °C while rotating and then quenched in air. This produced a homogeneous orange crystalline solid. IR and Raman spectroscopy were used to characterize the samples. The Raman spectrum for the 20% $SnI_2$ sample is shown along with other starting materials in Fig. (10).

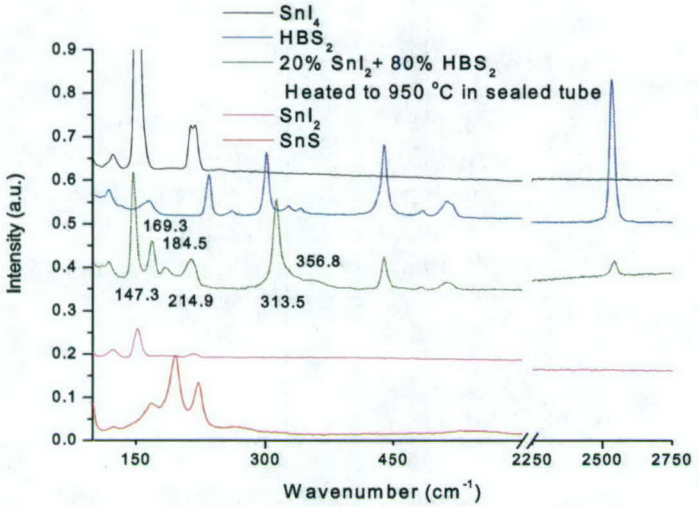


**Figure 10** Raman spectra of 20% $SnI_2$ + 80% $HBS_2$ is the middle green line. The other spectra are of the initial components $SnI_2$ and $HBS_2$ as well as SnS and $SnI_4$.

The Raman spectrum showed that there is a definite change in the structure when $SnI_2$ is added. There are several new peaks in this spectrum: 147, 169, 185, 215, and 313 $cm^{-1}$. The peaks at 147 and 215 $cm^{-1}$ are very close to the peaks in $SnI_4$ and therefore may indicate that some of the tin was converted to a tetrahedral coordination.

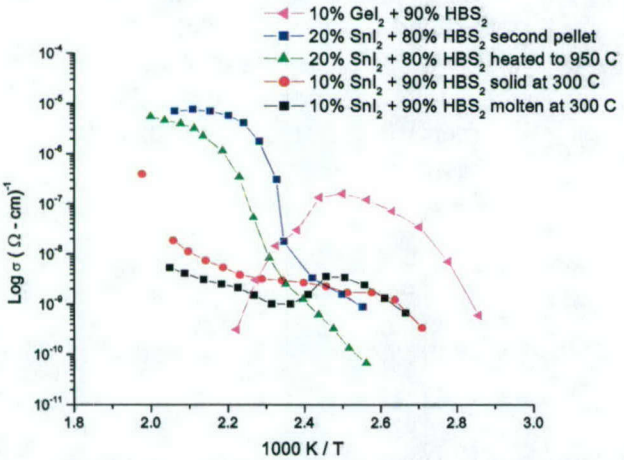


**Figure 11** Conductivities of various diiodide doped samples with metathioboric acid. The two tin samples are different pellets from the same batch. It's interesting to note the transition at about 140 °C in the 20% tin sample. It also appears as if there is a transition in the 10% solid portion at higher temperatures.

The conductivities of these samples show some very interesting properties. The left graph in Fig. (11) shows the conductivity of different samples while the graph on the right compares these conductivities to the samples without iodide salts. The $SnI_2$ sample has a conductivity of $5 \times 10^{-5}$ $(\Omega\text{-cm})^{-1}$ that is about two orders of magnitude greater than previous samples.

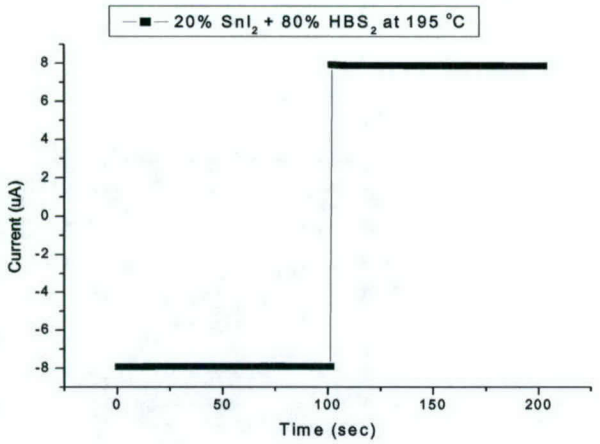


**Figure 12.** Polarization of the tin diiodide sample while held at 195 °C. The figure shows a very small time relaxation to the conduction phenomenon. This indicates a very fast protonic conduction or more electronic

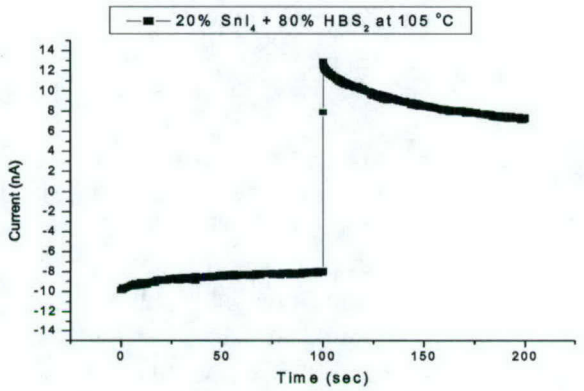


**Figure 13.** The polarization of a tin tetraiodide sample. This graph clearly shows time dependence to the conduction, which indicates a slower ionic conduction process. Also note that the current is three orders of magnitude lower than the previous $SnI_2$ sample.

### 3.1.3. $GeI_4 + HBS_2$ and $GeI_2 + HBS_2$

The samples in the series (x) $GeI_4$ + (1-x) $(HBS_2)_3$ with x = 0.1 and 0.2 have been prepared. The samples were sealed in a silica tube, ID = 8 mm OD = 12 mm, and placed in the box furnace. They were then heated to 280 °C at 1 °C/min. They formed very homogeneous melts at this temperature. The samples were then taken out of the furnace and air quenched. The samples looked like homogeneous crystals after cooling.

The samples in the series (x) $GeI_2$ + (1-x) $(HBS_2)_3$ with x = 0.1 and 0.2 have been prepared. The samples were sealed in a silica tube, ID = 8 mm OD = 12 mm, and placed in the box furnace. They were then heated to 250 °C at 2 °C/min and held for 0.5 to 2 hours. The quenched material did not appear to be completely homogeneous but it also did not appear to be fully crystalline. When quenched in water the samples appeared to almost have a glassy transparent nature. The conductivity of the x = 0.1 sample was shown in Fig. (11).

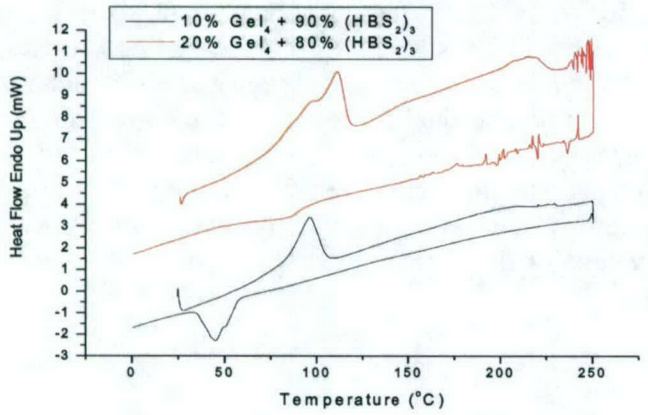


**Figure 14.** DSC scans of the two germanium tetraiodide samples. The samples show similar behavior to the tin tetraiodide samples. They have at least one melting point near 100 °C. However, the 20% $GeI_4$ sample shows very little crystallization and might be partially glassy.

### 3.2.CsI + $H_2S$ + $B_2S_3$ - Interstitial doping of CsI phases

This study was carried out see the effect of alkali halide on structure and proton conductivity. The samples with following compositions have been prepared and studied.

$$x\%CsI + (100\text{-}x)\%HBS_2 \rightarrow (100\text{-}x)/2\%\ [H_2S + B_2S_3] + x\%CsI, \text{ with } x = 5, 10, 20\%. \quad (10)$$

Fine powders of $HBS_2$ and $SiS_2$ or CsI are mixed, loaded in a silica tube, and sealed. The sealed tube was heated to about 500 to 700 °C depending on the composition of the mixture to obtain a uniform melt. The tube with molten mixture was then quenched in water to obtain protonated glassy or ceramic phases.

All the samples in the CsI doped system were crystalline. The IR spectra of all these samples are shown in Fig. (15). Two major IR bands are observed for thioborates; the band observed at 750 to 900 $cm^{-1}$ is due to trigonal borate units ($BS_{3/2}$) and the band at 950 to 1050 $cm^{-1}$ is due to thio-boroxol ring units ($B_3S_3S_{3/2}$). In meta thioboric acid $(HBS_2)_3$, one of the three sulfur atoms in a trigonal borate unit is non-bridging and hence the structural species involved are $BS_{2/2}SH$ and $B_3S_3(SH)_3$, respectively. The presence of protons in the materials is identified by the H-S stretch observed at 2530 $cm^{-1}$. The intensity of this peak is found to decrease (not shown) upon addition of CsI and is mainly due to decrease in $H_2S$ molar concentration. Some loss in proton concentration also occurs due to effects of heating thioboric acid to higher temperatures required to obtain uniform melt in the mixed systems. CsI is transparent to infrared wavelength region studied here (400 to 4000 $cm^{-1}$) and hence its structural details are not seen IR. CsI has a cubic structure like other alkali halides.

The intensity of thio-boroxol ring mode at 1020 $cm^{-1}$ decreases with the increase in CsI content in the system from 5 to 20 mol%. Although the samples in this system are crystalline, they are not stoichiometric compounds. Some structural disorder is still present in these samples as indicated by broad IR bands compared to crystalline $HBS_2$. A weak signature of tetrahedral borate groups is also observed at 720 $cm^{-1}$. However, the boron structure is predominantly in trigonal co-ordination with $BS_{2/2}SH$ units and $(B_3S_3)(SH)_3$ rings structures. In the binary cesium borate glass, the addition of cesium sulfide converts trigonal borate units to tetragonal units. Here in the ternary system, two types of structural modifications are possible for the reaction of $HBS_2$ with CsI, (i) cation displacement reaction between Cs and H with the formation of H-I and

cesium sulfide structures and (ii) interstitial doping of CsI in the network without altering the thioborate network structure, as it happens in silver iodide doped fast ion conducting samples. No evidence for H-I structures (observed at 2300 $cm^{-1}$) is seen in the IR spectra. If H-I structures have formed in the intermediate steps of the reaction and then decomposed, the corresponding concentration of cesium sulfide, which is thermally more stable, will be significant. This alkali sulfide would lead to change in coordination of borate units. However, the strength of the band due to $BS_4$ units is weak. This suggests that most of the CsI is interstitially doped in the borate network. Although CsI does not structurally modify the borate network it appears to help in proton conduction as explained in later sections.

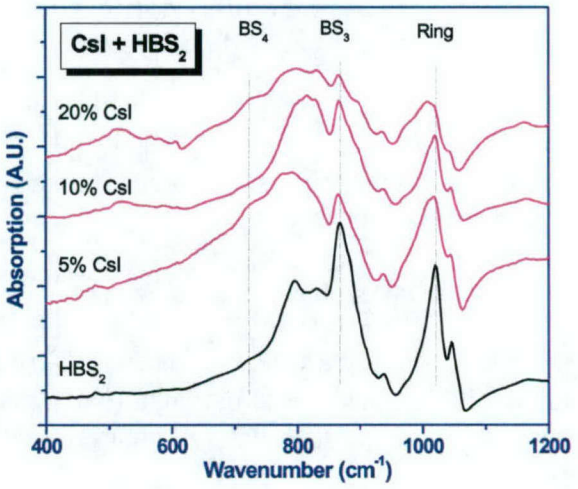


**Figure 15.**Infrared spectra of the samples in the $H_2S$ + $B_2S_3$ + CsI.

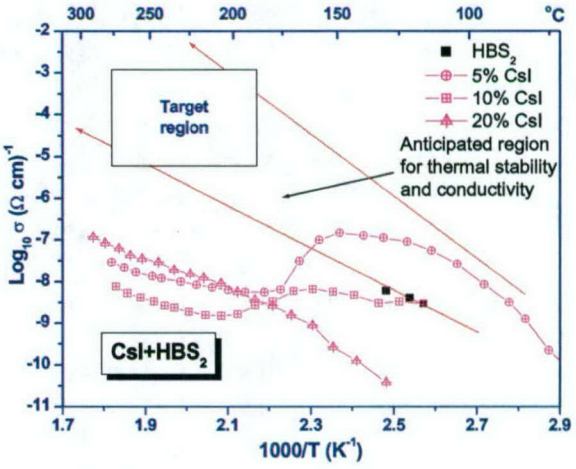


**Figure 16.** Proton conductivity of the samples in the $H_2S$ + $B_2S_3$ + CsI.

In Fig. (16), the temperature dependence of the conductivity is shown in the form of Arrhenius plots. The proton conductivity of the base materials $HBS_2$ is also shown for comparison. Although $HBS_2$ is rich in protons (50 mol % of $H_2S$), its conductivity is low. In addition, $HBS_2$ has lower melting point of about 130 °C and beyond this temperature loses most of its proton concentration due to its decomposition into $H_2S$ and $B_2S_3$. This results in a sudden drop in

conductivity. Again, noticeable conductivity only appears at higher temperature (around 250 °C) and is due to small concentration of protons present in the boron sulfide glass.

As shown, the proton conductivity is significantly influenced by structural modifications caused by the ternary additives CsI and $SiS_2$. About a two order of improvement in the conductivity is obtained with 5% addition of CsI. The thermal stability of the sample is also improved to about 150 °C. Beyond this temperature this sample looses protons and the conductivity falls. The sample with 10 % of CsI is found to be thermally stable up to a 160 °C; however the proton conductivity in this sample is about an order of magnitude less than that of the sample with 5% CsI. Higher CsI contents are required to improve the thermal stability of the sample above 200 °C. As shown, the sample with 20 mol. % of CsI has low proton conductivity at lower temperatures however it is thermally stable over a wider temperature range and reaches a higher proton conductivity of the order of $10^{-7}$ S/cm at a higher temperature of about 250 °C. The loss of proton conductivity at lower temperature is due to overall decrease in molar concentration of protons and also due to lose of some proton arising from the high melting temperature required for preparation of these samples as described earlier. The conductivity plots are not linear over the entire temperature range. However, the best fits in suitable temperature range were made to obtain activation energy. The activation energy for proton migration, obtained from the slope of these plots, is found to be ~ 0.8 to 1.2 eV (with an estimated error of about 10%). In CsI rich compounds some contribution to total ionic conductivity arises from cesium ions in the second thermal cycle owing to the formation of cesium modified glassy phases. However, the contribution to total conductivity by cesium ions is negligible in the first or following thermal cycles when the compound is not decomposed.

### 3.3. Complex ternary systems with structural modifications and mixed acids

#### 3.3.1. SrS + $HBS_2$

Structural modifications by alkaline sulfides such as SrS have also been carried out in details. Good improvement in proton conductivity were also obtained by reacting SrS with $HBS_2$ with liquid $H_2S$ at its vapor pressure according to,

$$SrS + 2(HBS_2)_3 \rightarrow (SH)_2(B_3S_3)\text{-}S\text{-}Sr\text{-}S\text{-}(B_3S_3)(SH)_2 + H_2S \qquad (11)$$

The reactions were aimed at bridging two thio-boroxol rings by strontium, as shown above. This expected to thermally stabilize the structure at higher temperature to obtain high proton migration. Although, some structural modification of the borate network and good improvement in conductivity was obtained, the reaction is far from complete. More reactions are being carried to improve the structural modification by more complete reaction.

#### 3.3.2. Mixed acids $HBS_2$ + $H_2Ge_4S_9$ systems

Protonated thioborogermanate phases were obtained by first reacting $H_2S$ with $GeS_2$ to form $H_2Ge_4S_9$ which was reacted with $HBS_2$ according to the following scheme:

$$y\ H_2Ge_4S_9 + (1\text{-}y)\ HBS_2 \rightarrow ((1+x)/2)\ H_2S + ((1\text{-}x)/2)\ B_2S_3 + (4x)\ GeS_2 \qquad (12)$$

One gram batches were prepared with, y = 0.08 and 0.17. These compounds required about 550-700°C for melting. The mixture were placed in a silica tube and sealed under vacuum. The tube was heated at the rate of 2°C/min then quenched in water. The samples in the series (y) $H_2Ge_4S_9$ + (1-y) $HBS_2$ formed a good melt around 550°C-700°C. The melt was dark and chocolate brown in color. The quenched sample was very close to the melt in color and porous glass in nature.

The IR spectra of samples in the (y) $H_2Ge_4S_9$ + (1-y) $HBS_2$ show H-S peaks at ~2530 $cm^{-1}$ indicating anhydrous protons present in the sample. The samples also show a band beginning at ~400 $cm^{-1}$. Based on previous studies of IR spectra of $\nu$-$B_2S_3$ and $HBS_2$ the peaks ~1000 $cm^{-1}$ is assigned to vibrational modes of six-membered rings. Similarly, trigonal units are visible in the spectra at ~900 $cm^{-1}$. Moderate oxide contamination was also detected in the spectra (~1200-1300 $cm^{-1}$). The ring mode decreases with addition of $H_2Ge_4S_9$. Further structural characterization of these samples and the preparation of more samples are under progress.

The temperature dependence of conductivity of the samples in this series is shown in Fig. (17). Conductivity plots of samples in this series show Arrhenius behavior (linear variation in log σ vs. 1000/T plots) with activation energy of 0.7 eV.

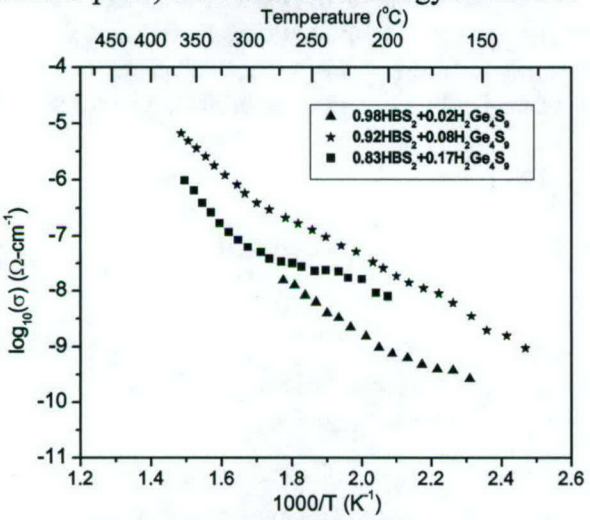


**Figure 17.** Proton conductivity of the samples in the series (y) $H_2Ge_4S_9$ + (1-y) $HBS_2$.

A preparation temperature as high as 700°C was required for melting the $0.17H_2Ge_4S_9$ + $0.83HBS_2$ compound. At such high temperatures the samples could react with silica and lose some proton content. It is unclear whether the temperature alone causes the reduction in $H_2S$ or if reaction time also plays a role in the process. The loss of protons is reflected in the transport properties of the sample with y = 0.17. Sample exhibiting prominent H-S peaks in IR spectra also showed higher proton conductivity.

### 3.3.3. CsSH + $HBS_2$ system

The structural modification of the borate network was also carried by reacting CsSH with thioboric acid. The reactions were carried out in two different ways. (i) The reactants were melted at 650 °C. Good melt was obtained at 650 °C and quenched in water. The IR spectrum

shows some structural modifications and also an increase in the oxide contamination. (ii) CsSH was reacted with $HBS_2$ in liquid $H_2S$ at its vapor pressure.

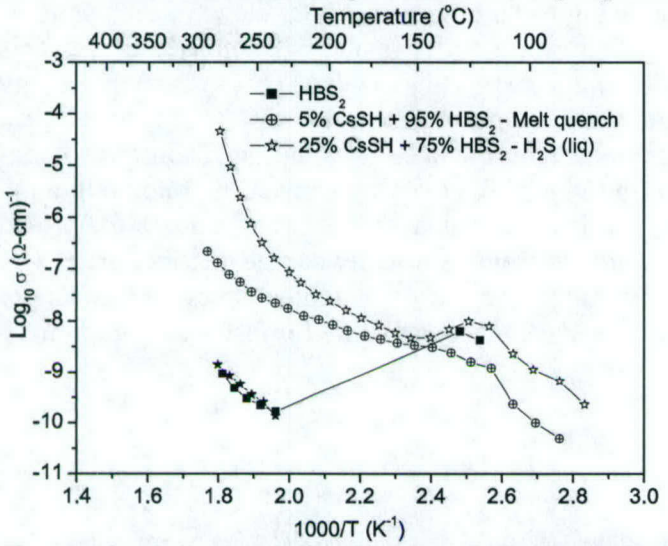


**Figure 18.** Proton conductivity of the CsSH + $HBS_2$ samples prepared by different methods.

The conductivity result for this sample is shown in Fig. (18). Although good improvement in conductivity is obtained, non-negligible contribution to conductivity from cesium is expected. The fraction of ionic conductivity due to cesium ion is not known at this time. Reactions are being carried out to prepare samples with minimal oxide contamination.

## 4. Discussion on proton conductivity

The present proton conductivity measurements were carried out in totally anhydrous environments using conductivity probes filled with helium. The measurement probes were also fitted with release valves to avoid pressure built up due to higher temperature and evolution of hydrogen sulfide. Hence no wetting of the samples from either hydrogen sulfide or water was allowed unlike hydrated membranes. In hydrated membranes fast proton conductivity is achieved below the steam point of $H_2O$ under conditions of saturated water vapors. The proton conductivity in the present anhydrous systems is expected to be higher under such pressurized conditions of hydrogen sulfide or other sources of anhydrous protons. The hydrogen bonding present in hydrated proton conductors is also absent in $H_2S$-based systems studied here. Note that the H-S-H bond angle is ~92° and is very close to the theoretical p-bonding value of 90° and in addition $H_2S$ has very low melting point of –82 °C compared to water. Hence the conducting species is not $H_3S^+$. Negatively charged thiol anion ($SH^-$) is a possible candidate for change transport. However our previous study of compositional dependence of conductivity in binary $H_2S$+$B_2S_3$ system and the corresponding physical and structural correlations does not corroborate with transport of $SH^-$ anions.

The proton migration in these systems is more likely to come from bare proton migration. This also supported by the weaker strength of H-S bond compared to H-O bond. However such migrations are not expected to be vacancy type and require support mechanisms. At lower temperatures, below 100 °C, no significant proton conductivity is observed and the samples are essentially insulating. At sufficiently higher temperatures, above 100 °C, although the protons are strongly bonded to the sulfur atom, enough thermal energy is available to cross the potential

barrier and enable proton migration to occur. A bond-making and bond-breaking type of mechanism for proton migration is proposed. A proton bonded to a non-bridging sulfur atom breaks its bonding and jumps out of its site owing to its higher energy at elevated temperatures and then bonds to a neighboring sulfur atom which was a bridging site in its immediate past. This process is expected to have higher activation energy. Note that the activation energy experimentally observed are higher and are in the range of 0.8 to 1.2 eV. This type of bond reorganization requires an optimum balance between protonated sites and availability of bond-making sites in its immediate neighborhood. In CsI doped ternary systems such proton migration is further supported by larger iodide anions, which serve as a "hitchhiking" centers for proton migration owing to their shallower potentials arising from their wider charge distribution. Hence it is important to create HX doped structures in these types of materials. These materials are expected to have very high proton concentrations and suitable structure for fast proton migration.

## 5. Products of the Research Project

### i. Publications resulting from the Research Project

1. Karthikeyan, Annamalai, Martindale, Chad, Martin, Steve W., "Preparation and Characterization of New Proton Conducting Chalcogenide Glasses," The Proceedings of the 16th University Conference on Glass, Rensselaer Polytechnic Institute, Troy, NY, August 13-15, 2003, Journal of Non-Crystalline Solids, Vol. 337 pp. 166-173, 2004.
2. Karthikeyan, Annamalai, Chad A. Martindale and Steve W. Martin, , "Proton conductivity in a new class of $H_2S$ modified thioborate based glasses and ceramics," Proceeding of the 14th International Meeting on Solid State Ionics, Monterey, CA, June 22 - 27, 2003, Solid State Ionics, Vol. 175, pp. 655-659, 2004.
3. Karthikeyan, Annamalai, Chad A. Martindale, Steve W. Martin, "New Anhydrous Proton Conducting Materials Based on Thioborates," Physics and Chemistry of Glasses, Proceedings of the "4th International Conference on Borate Melts, Crystals, and Glasses," Cedar Rapids IA, July 24-26, 2002, (2003), Vol. 44, no.2, pp. 143-146, 2003
4. Karthikeyan, Annamalai, Chad A. Martindale, Steve W. Martin, "New protonated glasses in the $xH_2S + (1-x)B_2S_3$ Series," Journal of Physical Chemistry B, Vol. 107, pp. 3384-3389, 2003.
5. Karthikeyan, Annamalai, Chad A. Martindale, Steve W. Martin "A New Method to Prepare Polycrystalline Meta-Thioboric Acid, $(HBS_2)_3$," Inorganic Chemistry, Vol. 41(4), 622-624, 2002.

### ii. Technical Presentations Resulting from the Research Project

1. "New Protonated Thioborate Glasses and Glass-Ceramic Materials," (poster with Annamalai Karthikeyan, and Chad A. Martindale) 104th Annual Meeting of the American Ceramic Society, St. Louis, MO, April 2002
2. "Development of New Fast Proton Conducting Chalcogenide Glassy Electrolytes ," Office of Naval Research and Air Force Office of Scientific Research, Electrochemistry Program review Meeting, Washington, D.C., February 2000.

**iii. Invited Technical Presentations Resulting from the Research Project**

1. "Preparation and Characterization of New Proton Conducting Chalcogenide and Oxy-Chalcogenide Solid Electrolytes for PEM Fuel Cells," Department of Materials Science and Engineering, Global Fuel Cell Research Center, University of Connecticut, December 15, 2003
2. "Preparation and Characterization of New Proton Conducting Chalcogenide and Oxy-Chalcogenide Solid Electrolytes for PEM Fuel Cells," Chalmers University of Technology, Department of Applied Physics, January 30, 2004
3. "Synthesis and Characterization of a New Class of Ceramic Intermediate Temperature Proton Conducting Alkali Thiohydroxometallate Membranes for use in Proton Exchange Membrane Fuel Cells," NorFA Summer School on New Materials and Technologies for Low Temperature Fuel Cells, Smögen, Sweden, August 12-15, 2004.

**iv. Records of Invention Resulting from the Research Project**

1. "Fast Proton Conducting Chalcogenide Glasses," Record of Invention, Steve W. Martin, ISURF # 02553, February, 1999.

**v. Graduate Student Theses Resulting from the Research Project**

1. Chad Martindale, "Development of New Anhydrous Proton Conducting Materials Based on Chalcogenide Glasses," Ph. D., Department of Materials Science & Engineering, Iowa State University, In progress, graduation expected December 2005.